Short communication

A novel boost circuit design and in situ electricity application for elemental sulfur recovery

CrossMark

Jia Liu, Yujie Feng*, Weihua He, Yuanyuan Gong, Youpeng Qu, Nanqi Ren

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No 73 Huanghe Road, Nangang District, Harbin 150090, China

HIGHLIGHTS

- A novel microbial electrochemical system (MES) was designed for electricity generation and sulfate conversion.
- Both electrical energy boosting and in situ utilization were achieved by using novel boost circuit.
- Elemental sulfur can be recovered from an electrochemical deposition cell (ECD) without any net energy input.

ARTICLE INFO

ABSTRACT

A novel system containing a microbial electrochemical system (MES) for electricity generation and sulfate conversion, a novel boost circuit (NBC) for in situ utilization of the electrical energy and an electrochemical deposition cell (ECD) to recover sulfur in water is designed and established. This combined system has a higher energy utilization efficiency of 63.6% than that of conventional sulfate reduction reactors with an elemental sulfur recovery efficiency up to $46.5 \pm 1.5\%$ without net energy input. This system offers a promising, and cost-effective approach for sulfate wastewater treatment.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Sulfate contamination is present in a wide range of both industrial wastewaters and sewage such as mining, tannery, food processing, paper mill wastewaters etc [1,2]. In wastewater treatment plant (WWTP), sulfate compounds were usually converted to sulfide or hydrogen sulfide by sulfate-reducing bacteria (SRB) under anaerobic conditions of wastewater treatment process and released to air, causing secondary pollution [3]. These compounds emission are associated with several important deterioration problems for aquatic ecosystems, including release of unpleasant odors, pose a potential risk to human health and induce corrosion to architectures, metals etc [4,5]. So, the removal of sulfate from wastewaters and recovery of elemental sulfur are two key challenges that researchers should be faced with.

Sulfate can be removed by physico-chemical methods, but high operation cost and post-treatment of large quantities of sludge restrained the utilization of physico-chemical technologies to collect sulfur [3]. During biological removal process, sulfate is usually converted to sulfide coupling with COD removal by strains of sulfate-reducing bacteria (SRB). Elemental sulfur might be further collected by strains of sulfur-oxidizing bacteria (SOB) [6]. However, it is difficult to separate the elemental sulfur from activated sludge although the activities of both SRB and SOB are high in practical WWTP [7]. Moreover, both high running cost (€ 1.9 to 7.2 kg^{-1} S removal), low energy utilization efficiency (10%–25%) and low sulfate removal rate (26.4%–52.9%) are a major bottleneck for the existing sulfate removal technologies [3,8–10].

The electrochemical deposition of sulfide can be used to recover pure elemental sulfur on the surface of electrode [11]. It offers very beneficial alternative and promising approach to improve recovery efficiencies of elemental sulfur and enable the development of new processes to minimize by-products and large scale production [1,12]. But the major limitation of the

---

* Corresponding author. Tel./fax: +86 451 86287017.
  E-mail address: yujief@hit.edu.cn (Y. Feng).
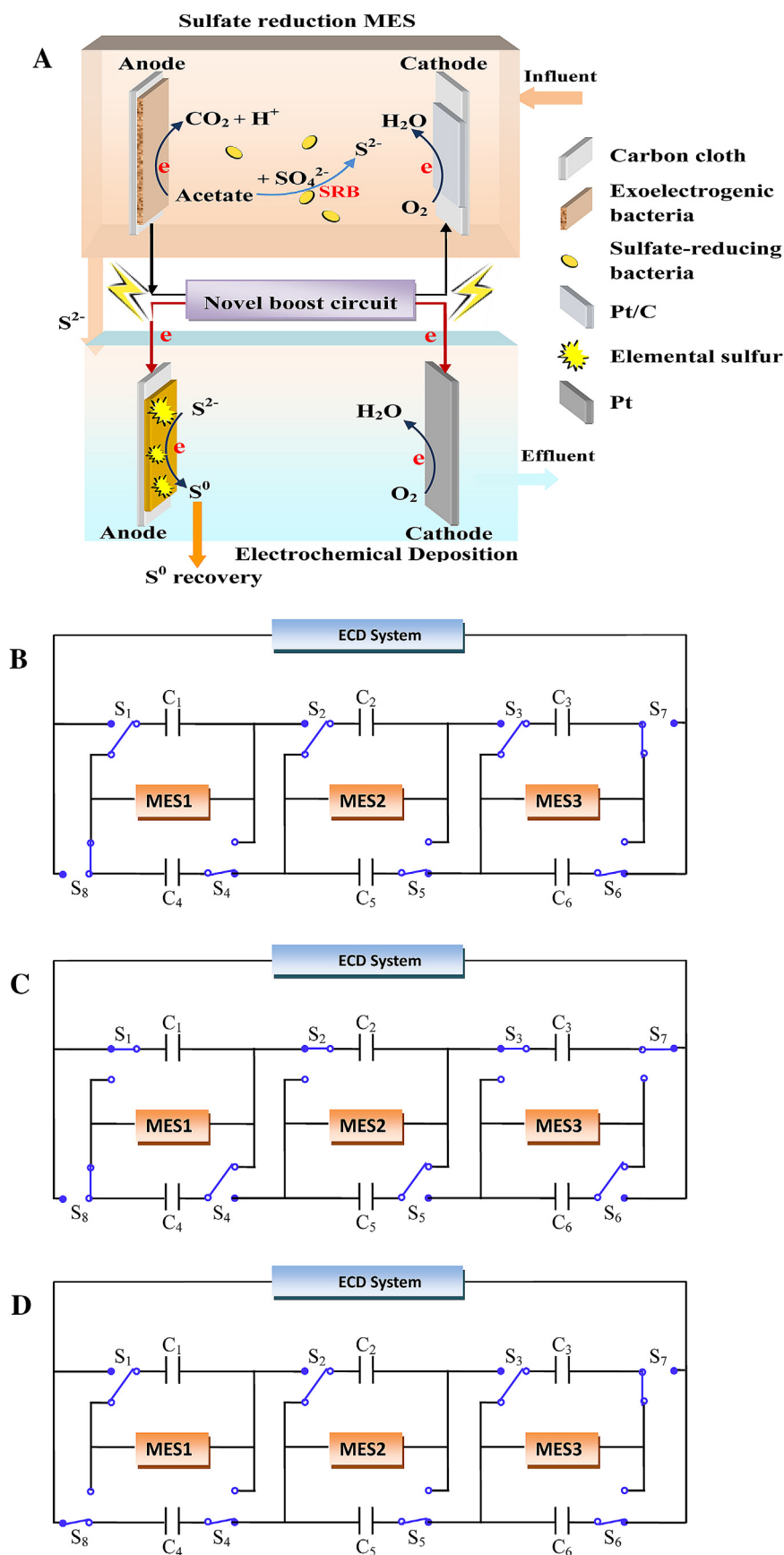
Fig. 1. The schematic (A) and circuitry diagrams of in-situ energy-harvesting and utilization based alternate charging and discharging of both sulfate reduction MESs and electrochemical deposition system: (B) charging of C_1–C_3 by MES1–MES3, (C) discharging of C_1–C_3 capacitors in series and charging of C_4–C_6 by MES1–MES3, (D) discharging of C_4–C_6 capacitors in series and charging of C_1–C_3 (MES1, MES2, MES3, sulfate reduction MESs; ECD system, electrochemical deposition system; C_1–C_6, external capacitors; S_1–S_8, relay switches).

electrochemical deposition is the high energy consumption due to the consumption of external power.

Microbial electrochemical system (MES) is a novel bio-electrochemical system that can convert chemical energy from wastewater directly into electricity using exoelectrogenic micro-organisms as catalysts [13]. It has been proved enormous potential advantages in wastewater treatment field due to its direct harvesting of electricity and less energy input [14,15]. Theoretically, sulfate can be reduced to sulfide in MES if strains of SRB existed in the system [16,17]. Our previous research also indicated that sulfide can also be oxidized into elemental sulfur and easily deposited on the anodic surface. The precipitated elemental sulfur on the anode surface was hard to be recovered and might incur an anodic passivation over long time operation, as well as inhibition of exoelectrogenic bacteria activity by the high sulfide concentration [18,19].

Therefore, in order to achieve the simultaneous effective treatment of sulfate and high elemental sulfur recovery efficiencies, here in this paper, a new system was designed, consisted of a) MES to generate electricity, b) a novel boost circuit (NBC) consists of supercapacitors to collect and boost the voltage as a power supply and c) an ECD (Electrochemical Deposition) to realize the sulfur recovery without external energy input. In this energy coupling system, the energy needed for elemental sulfur recovery in ECD was supplied by the oxidation of pollutants in wastewater in MES. Compared with the conventional sulfate reduction reactors, the novel energy coupling system has the advantages of high sulfate reduction rate, high elemental sulfur recovery, and without any net energy input. Thus, this system is newly designed with an environmental friendly electrochemical technology and further promising cost effective approach for practical sulfate wastewater treatment.

2. Materials and methods

2.1. The combined system construction

The present system consists of three MES reactors, novel boost circuit (NBC), one electrochemical deposition system (ECD) (Fig. 1).

MES was consisted of Lexan cubic blocks with cylindrical chambers inside (3 cm in diameter and 4 cm in length, net volume 28 mL) [20]. The anodes were made of non-wet proofed carbon cloth (E-TEK, USA). Carbon cloth (CC, B-1 Designation B, 30% PTFE-based wet proofed, Clean Fuel Cell Energy, LLC, USA) coated with Pt/C catalyst (0.35 mg Pt/C cm^{-2}, Nafion binder) was used as air cathodes.

The novel boost circuit (NBC) was composed of six super-capacitors (3.3 F), three timing relays, 8 switches and connection circuits (equivalent circuit shown in Fig. 1B–D). Each MES respectively corresponded to two capacitors. The switchover of charging and discharging for each pair of supercapacitors was controlled by the unified mode of the timing relays.

The electrochemical deposition system (ECD) consisted of an anode, a cathode and the electrolyte with a net volume of 28 mL. Carbon cloth (projected area of 7 cm^2, E-TEK, USA) was used as working electrode, while platinum was used as the counter electrode.

2.2. The combined system operation

The triplicate MESs were inoculated with the effluents from other MES, which were stably operated for more than one year. All the MESs operated in fed-batch mode at 1000 Ω external resistor (unless otherwise specified) in a constant temperature room (30 °C). After three successive batch cycles of reproducible voltage generation, the MESs were inoculated with a 30:70 mixture of the pre-acclimated suspension of SRB and synthetic sulfate medium in the following three batch cycles. The medium contained 2 g L^{-1} of CH$_3$COONa, 1 g L^{-1} Na$_2$SO$_4$, 50 mmol L^{-1} PBS, 12.5 mL L^{-1} mineral, and 5 mL L^{-1} vitamin solutions. The influent was fed into the three MES reactors one by one with a time interval of 16 h. The operation period of each MES reactor was set at 48 h. The effluent from each MES reactor was fed into the ECD with the same interval of 16 h.

2.3. Calculations and measurements

The voltage of MES, voltage drop of the capacitor, and the input voltage of electrochemical systems were recorded per 30 min (unless otherwise specified) by the data acquisition system (PISO-813, ICP DAS Co., Ltd.). The 30 min average data was automatically calculated based on the last 30 original data of 1 min. The 30 min average data were used in most of the figures. COD removal rate, CE, energy and energy conversion efficiency were calculated as previously described [20,21,22]. The concentration of both sulfate and sulfide were measured by ion chromatography (Dionex ICS-3000) [18], the generation of elemental sulfur was measured by spectro-photometric method [23].
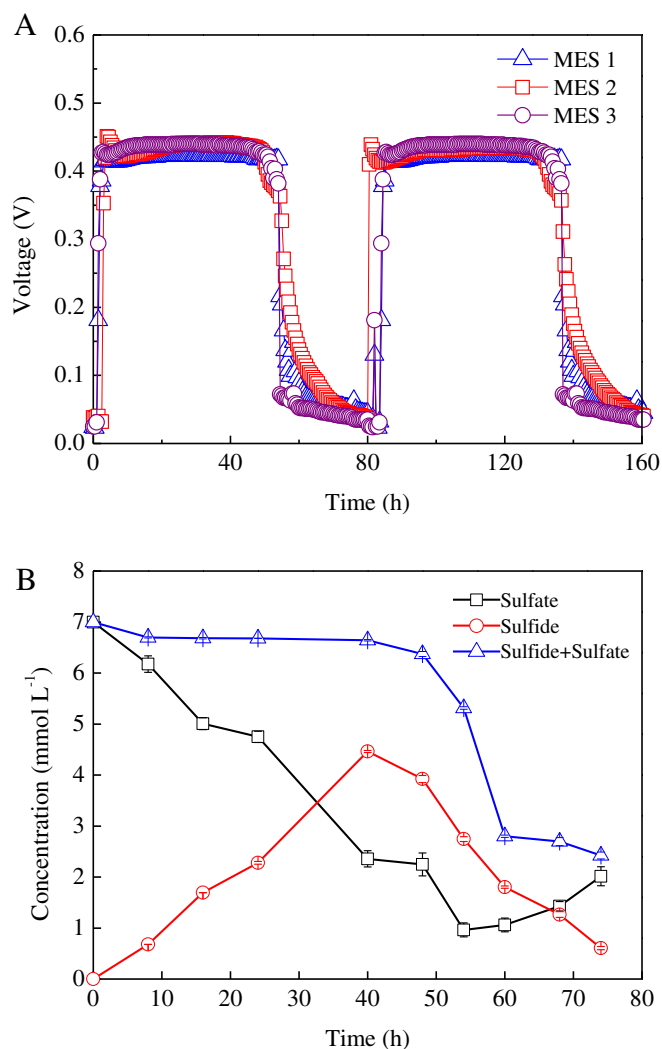

Fig. 2. The voltage output (A), change in concentration of sulfate, sulfide with time during a complete cycle in MES (B).

3. Results and discussion

3.1. The novel boost circuit

The novel boost circuit (NBC) was constructed by supercapacitor arrays. Six capacitors were charged by three MESs, with two capacitors alternatively charged by one MES. The charging characteristic of novel boost circuit (NBC) was examined over 80 min with an MES as the power supply (Fig. S1A). The voltage of the capacitor increased fast in the first 30 min. Afterward the voltage increased slowly, indicated a saturation region. The maximum charging efficiency was 84% at 30 min. Fig. S1B showed the discharging characteristic of the capacitor valued 3.3 F was investigated under 30 min discharging times. Although the discharging phase of the capacitor was affected by the target of the discharging times, however, considering the matching of total charge and discharge times, 30 min were determined as both the charging and discharging periods.

Three capacitors (C_1–C_3) was charged by 30 min using three MES (MES1, MES2, MES3) (Fig. 1B), and then they were discharged in series to power the electrochemical deposition reactor (ECD) in the following 30 min, while another three capacitors (C_4–C_6) were charged by the three MESs (MES1, MES2, MES3) simultaneously (Fig. 1C). When capacitors (C_4–C_6) were discharged in series to supply energy to electrochemical deposition reactor (ECD), capacitors (C_1–C_3) were recharged by three MESs again (Fig. 1D).

3.2. MES performance

Stable voltages (440 ± 10 mV, 1000 Ω, over 48 h) from three parallel MESs (MES1, MES2, MES3) were observed after the inoculation of SRB in two consecutive cycles (Fig. 2A), indicated that both anodic exoelectrogenic bacteria and SRB communities had been well acclimated in MESs.

Repeatable cycles of the sulfate reduction were also observed simultaneously with the stable power generation of MESs, indicated that the SRB had the better adhesion property of the rougher anode and vessel wall of reactor. The sulfate contents of MESs were decreased at near linear rate from 7.0 to 1.0 mmol L^{-1} during 0–52 h (Fig. 2B). The maximum sulfate removal rate of 86.3% was achieved at 52 h, followed by a slow increase in sulfate concentration of the effluent at the end of the period. The increase of sulfate in the effluent could be attributed to the relative positive anode potential caused by the competition of sulfide oxidation process at the end of the cycle, with a part of sulfide oxidized to sulfate [24]. Sulfide was simultaneously accumulated until a peak concentration of 4.5 ± 0.02 mmol L^{-1} observed at 40 h and then decreased to 0.61 ± 0.03 mmol L^{-1} during the rest of the cycle. The total dissolved sulfide and sulfate was sharply decreased from 6.3 ± 0.05 to 2.8 ± 0.02 mmol L^{-1} during 48–60 h. And then it was slowly decreased to 2.4 ± 0.06 mmol L^{-1} within the next 15 h, which was consistent with the trend of power output. The decrease of total dissolved sulfide and sulfate was partly due to the conversion of sulfide to element sulfur on the anode (Fig. S2).
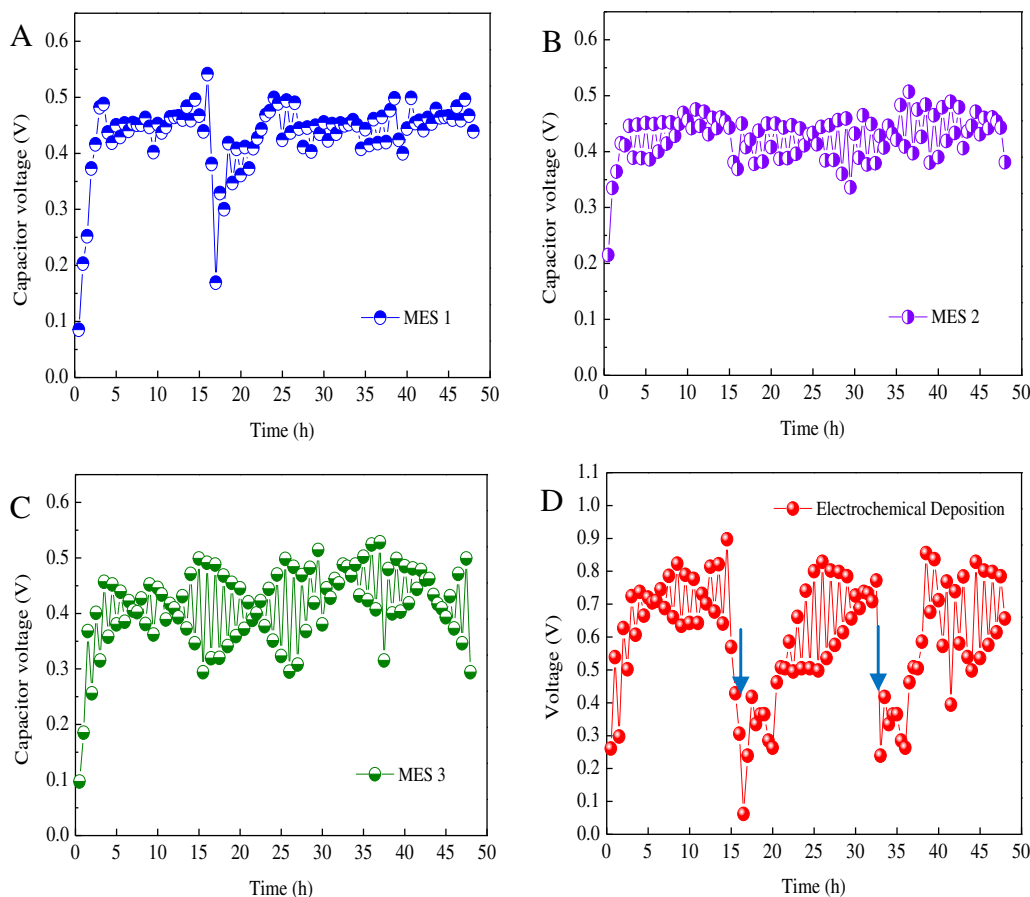
Fig. 3. The voltages of the capacitors using MES as power supply (A–C), and the input voltages of electrochemical deposition system (D). (A) MES1, output voltage of C_1 and C_4 by MES1; (B) MES2, output voltage of C_2 and C_5 by MES2; (C) MES3, output voltage of C_3 and C_6 by MES3. The blue arrows indicate the effluent of ECD was replaced with fresh MES-effluent water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Since the voltage of MES began to decrease at 48 h, the total charging time for capacitors was determined as 48 h to obtain a high power supply. The effluent from MES that capable to reduce sulfate was transferred to an ECD reactor at 48 h in order to minimize losses on deposition of elemental sulfur on the anode of MES, which meets the expectation of elemental sulfur recovery.

3.3. Both performance and energy efficiency of the combined system

Variations of both voltages across MESs to power capacitors and the discharging voltages of capacitors to supply to ECD reactor were shown in Fig. 3. The oscillation of voltages of both capacitors and ECD were probably due to the high switching frequency of charging and discharging processes. The average voltages produced by the sulfate reduction MESs were: 0.45 ± 0.03 V (MES1, Fig. 3A); 0.43 ± 0.04 V (MES2, Fig. 3B); 0.41 ± 0.04 V (MES3, Fig. 3C), supplying total energies to NBC of 30.4 J (MES1); 29.0 J (MES2); 27.8 J (MES3). The total energy conversion efficiency of the capacitors connected to the sulfate reduction MESs can be calculated as 82.5% based on total energy produced in MESs. The results indicated that the present NBC by using capacitor arrays was a promising method to achieve a high energy harvesting efficiency.

The voltage supplied to electrochemical deposition system was 0.76 ± 0.15 V, which can be used to drive this thermodynamically unfavorable reaction of oxidizing sulfides to elemental sulfur. The changes of sulfide concentration in the ECD system over time were shown in Fig. S3. The sulfide concentration was gradually reduced

at near linear rate from 4.0 to 0.6 mmol L^{-1} during 0–16 h, indicating that the electrolyte in ECD reactor was replaced with effluent of MES every 16 h (Fig. 3D). The total energy consumed in electrochemical deposition system was 62.7 J. And the total energy efficiency from the generation (MES) to final utilization (ECD) was calculated as 63.6%.

3.4. COD removal rates, Coulombic efficiency and elemental sulfur recovery rate

COD removal rates and Coulombic efficiency (CE) were $82.3 \pm 0.3\%$ and $35.8 \pm 0.8\%$ as listed in Fig. 4A, indicated that MESs utilized here can be stably operated under NBC environment to sustain an energy harvesting. The Coulombic efficiency was calculated under the maximum power output point by optimizing the external resistance.

The sulfate removal rate reached $90.2 \pm 1.2\%$ and elemental sulfur recovery rate reached $46.5 \pm 1.5\%$ (Fig. 4B). The high sulfate removal rate strongly depended on the activity of SRB in MES while the elemental sulfur recovery rate depended on the electrochemical sulfur deposition rate. The COD/sulfate ratio could also affect the coulombic efficiency and the theoretical sulfur recovery rate in the coupling system. Based on the coulombic efficiency in MESs and the coulombic transfer efficiency from capacitors to ECD, the COD/sulfate ratio (2.3:1) in this study could be too low to adequately supply power for ECD to recover all the sulfur. This implies that sulfate wastewater with higher COD/sulfate ratio could effectively achieve sulfur removal and elemental sulfur recovery in the energy coupling system. Moreover, the electrical energy stored in the capacitors can achieve the in situ utilization of energy recovered from sulfate wastewater. Therefore, the MES and electrochemical coupled design can be used to promote the sulfate-containing wastewater treatment.

4. Conclusions

A novel energy coupling system was designed for sulfate reducing, energy boosting and in-situ application as power supply on ECD to achieve elemental sulfur recovery without any net energy input. The energy efficiency of the whole system was 63.6% and the maximum elementary sulfur recovery rate was $46.5 \pm 1.5\%$. During the treatment process, the coupling system needs precise operation to match the MES and ECD in both matter and energy aspects. However, the coupling system provides a promising alternative bio-treatment process of sulfur wastewater with the advantages of in-situ utilization of energy recovery, high efficiency of pollutant removal and high ratio of elemental sulfur recovery.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.09.098.
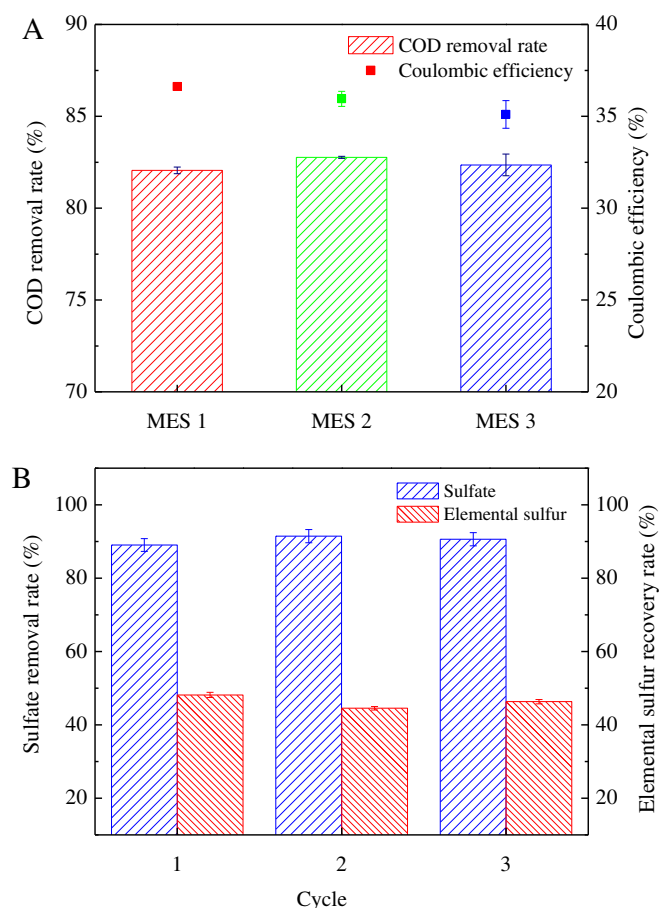

Fig. 4. The Coulombic efficiencies, COD remove rate (A) and sulfate removal rate, elemental sulfur recovery rate (B) of overall systems.

References

[1] P.K. Dutta, K. Rabaey, Z. Yuan, R.A. Rozendal, J. Keller, Water Res. 44 (2010) 2563–2571.

[2] F. Liang, Y. Xiao, F. Zhao, Chem. Eng. J. 218 (2013) 147–153.

[3] L. Zhang, P. De Schryver, B. De Gusseme, W. De Muynck, N. Boon, W. Verstraete, Water Res. 42 (2008) 1–12.

[4] F. Zhao, N. Rahunen, J.R. Varcoe, A. Chandra, C. Avignone-Rossa, A.E. Thumser, R.C. Slade, Environ. Sci. Technol. 42 (2008) 4971–4976.

[5] P. Lens, L. Pol, IWA, London, 2000.

[6] K. Tang, V. Baskaran, M. Nemati, BioChem. Eng. J. 44 (2009) 73–94.

[7] M.A.M. Reis, J.S. Almeida, P.C. Lemos, M.J.T. Lemos, Biotechnol. Bioeng. 40 (1992) 593–600.

[8] R. Liu, C.Y. Gao, Y.G. Zhao, A.J. Wang, S.S. Lu, M. Wang, F. Maqbool, Q. Huang, Bioresource Technol. 123 (2012) 86–91.

[9] L. Montoya, L.B. Celis, M. Gallegos-Garcia, E. Razo-Flores, A.G. Alpuche-Solis, Eng. Life Sci. 13 (2013) 302–311.

[10] L. Piet, W. Peter, H. Marianne, M. Angelo, IWA Publishing, 2005, p. 385.

[11] P.K. Dutta, K. Rabaey, Z. Yuan, J. Keller, Water Res. 42 (2008) 4965–4975.

[12] I. Pikaar, R.A. Rozendal, Z. Yuan, J. Keller, K. Rabaey, Water Res. 45 (2011) 5381–5388.

[13] F. Harnisch, U. Schroder, Chem. Soc. Rev. 39 (2010) 4433–4448.

[14] R.A. Rozendal, H.V. Hamelers, K. Rabaey, J. Keller, C.J. Buisman, Trends Biotechnol. 26 (2008) 450–459.

[15] B.E. Logan, Nat. Rev. Microbiol. 7 (2009) 375–381.

[16] M. Sun, Z.H. Tong, G.P. Sheng, Y.Z. Chen, F. Zhang, Z.X. Mu, H.L. Wang, R.J. Zeng, X.W. Liu, H.Q. Yu, L. Wei, F. Ma, Biosens. Bioelectron. 26 (2010) 470–476.

[17] K. Rabaey, K. Van de Sompel, L. Maignien, N. Boon, P. Aelterman, P. Clauwaert, L. De Schamphelaire, H.T. Pham, J. Vermeulen, M. Verhaege, P. Lens, W. Verstraete, Environ. Sci. Technol. 40 (2006) 5218–5224.

[18] P.K. Dutta, J. Keller, Z. Yuan, R.A. Rozendal, K. Rabaey, Environ. Sci. Technol. 43 (2009) 3839–3845.

[19] F. Zhao, N. Rahunen, J.R. Varcoe, A.J. Roberts, C. Avignone-Rossa, A.E. Thumser, R.C. Slade, Biosens. Bioelectron. 24 (2009) 1931–1936.

[20] J. Liu, Y.J. Feng, X. Wang, X.X. Shi, Q. Yang, Z.H. Zhang, N.Q. Ren, J. Power Sources 196 (2011) 8409–8412.

[21] J. Liu, Y.J. Feng, X. Wang, Q. Yang, X.X. Shi, Y.P. Qu, N.Q. Ren, J. Power Sources 198 (2012) 100–104.

[22] H. Wang, J.D. Park, Z. Ren, Environ. Sci. Technol. 46 (2012) 5247–5252.

[23] J.K. Bartlett, D.A. Skoog, Anal. Chem. 26 (1954) 1008–1011.

[24] Pourbaix, Pergamon, Oxford, 1966.